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Hydriding of Mg_2Ni in Ammonia

V. N. Fokin, E. E. Fokina, and B. P. Tarasov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, pr. Akademika Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: fvn@icp.ac.ru

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Abstract—The chemical interaction between the intermetallic compound Mg_2Ni and ammonia in the presence of NH_4Cl as an activator is investigated at temperatures from 100 to 450°C, and the reaction scheme is presented. The results demonstrate that the use of ammonia for hydriding/nitriding the intermetallic compound makes it possible to prepare various magnesium compounds (Mg_2NiH_4, Mg_3N_2, and $Mg(NH_2)_2$) in a highly dispersed state.

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INTRODUCTION

The large weight percentage of hydrogen (7.6 wt %) in MgH_2 and the high volumetric density of hydrogen in this hydride (120 kg/m^3) make it an attractive material for hydrogen storage systems [1]. At the same time, the high temperature of the hydriding/dehydriding reactions and the considerable energy required for dehydriding pose serious problems for the practical application of magnesium hydride in hydrogen fuel cells. It is known that these problems can, in principle, be resolved by taking advantage of one of the classic approaches in materials research—by alloying the hydride-forming metal Mg with another metal, T, that is nonreactive with hydrogen under normal conditions, to give a binary intermetallic compound, e.g., Mg_2T. The hydriding of such compounds is, in most cases, a reversible process and has the advantages of lower temperatures and more favorable thermodynamic parameters in comparison with Mg hydriding.

Mg_2Ni and multicomponent alloys containing it hold a special position among Mg_2T-type intermetallics, and the hydriding of such alloys has been the subject of intense research [2–4].

The intermetallic compound Mg_2Ni forms peritectically at 760°C and has a hexagonal structure with lattice parameters $a = 0.519–0.521$ nm and $c = 1.321–1.325$ nm [5]. After grinding to a particle size of ≈200 μm and degassing for 1 h at 250°C, it reversibly reacts with high-purity hydrogen at pressures from 1 to 5 MPa and temperatures from 150 to 200°C, without disproportionation, to form a hydride of composition Mg_2NiH_4 [4, 6–8]. According to X-ray diffraction data, this hydride crystallizes in monoclinic symmetry with lattice parameters $a = 1.32$ nm, $b = 0.64$ nm, $c = 0.65$ nm, and $\beta = 93.25°$. In an inert atmosphere, Mg_2NiH_4 decomposes at 255°C, releasing all of the hydrogen, with no changes in the metal matrix, which retains its ability to absorb hydrogen. Zaluska et al. [9] reported that this hydride in a nanoparticulate state had a reduced decomposition temperature (by 50–60°C).

As part of our studies concerned with the use of ammonia for hydriding, hydriding/nitriding, and dispersing intermetallic compounds [10, 11], this paper presents an experimental study of the behavior of the intermetallic compound Mg_2Ni in ammonia in a wide temperature range in the presence of ammonium chloride as a reaction activator.

EXPERIMENTAL

Starting reagents. Alloys for this investigation were prepared from 99.99%-pure nickel and 99.95%-pure magnesium. The starting mixture was melted in a vacuum induction furnace under a molten eutectic LiCl–KCl flux. The alloy composition was determined by chemical analysis and X-ray diffraction. According to the elemental chemical analysis data, the alloy had the composition $Mg_{1.95}Ni$. The chlorine content was below 0.5%. According to the X-ray diffraction results, the alloy was single-phase: all of the observed diffraction peaks could be indexed in a hexagonal structure with lattice parameters $a = 0.5215$ nm and $c = 1.325$ nm, in good agreement with previous results [5]. Immediately before characterization, the oxide film on the surface of the alloy was removed abrasively, and the alloy was washed with ethanol and diethyl ether, ground in an argon atmosphere, and sieved to a particle size less than 200 μm. The specific surface area S of the resultant powder was 0.04 m^2/g.

Ammonium chloride (reagent grade) was vacuum-dried at 150°C for 9 h. The purity of the ammonia after drying over sodium metal was 99.99%.

Experimental procedure. The chemical interaction between Mg_2Ni and ammonia (hydriding/nitriding process) was studied in a 60-ml high-pressure laboratory apparatus at an initial ammonia pressure of 0.6–0.8 MPa, using ammonium chloride (10 wt % relative to the intermetallic compound) as a reaction activator. A weighed amount (1.0–1.5 g) of the starting mixture was loaded into a stainless-steel container, which was then mounted in an autoclave. After pumping to a residual pressure of $\simeq 1$ Pa at $\simeq 20°C$ over a period of 30 min, the autoclave was charged with NH_3 to a pressure of 0.6–0.8 MPa and left standing at this temperature for 30 min. Next, the reactor was heated to a preset temperature, held there for 3 h, cooled to $\simeq 20°C$, and heated again. Since the pressure in the system increased during the reaction owing to hydrogen and nitrogen release (no more than 1.5 MPa), the process was considered to reach completion when the pressure stopped varying. After an appropriate number of heating–cooling cycles, the ammonia was discharged to a buffer tank, and the reaction products were drawn from the reactor in an inert atmosphere and analyzed.

The NH_4Cl was removed from the hydriding/nitriding products by washing with ethanol or evacuation [11].

Characterization and chemical analysis. X-ray diffraction patterns were collected on an ADP-1 computer-controlled diffractometer (CrK_α radiation).

The specific surface area of the samples was evaluated using the BET equation from low-temperature krypton adsorption measurements after degassing the solid phase in a vacuum of 1.3×10^{-3} Pa at 300°C for 15 h. The error of determination was within 10%.

Thermal analysis was carried out with a Netzsch STA 409 Luxx simultaneous thermal analyzer (TG–DTA/DSC) in flowing argon at a heating rate of 10°C/min.

The hydrogen content of the reaction products was determined by a standard procedure, by burning samples in flowing oxygen. Nitrogen was determined by the Kjeldahl method, and chlorine was determined turbidimetrically.

RESULTS AND DISCUSSION

The Mg_2Ni–ammonia reaction conditions and the results obtained are summarized in the table.

At 100°C, the intermetallic compound shows little or no visible reaction with ammonia, but ammonia exposure increases the specific surface area of Mg_2Ni by several orders of magnitude, from 0.04 to 14.7 m^2/g, and, according to X-ray diffraction results, slightly changes its lattice parameters (sample 1). Raising the temperature to 150°C (sample 2) leads to hydrogen uptake and the formation of an $Mg_2NiH_{0.3}$ solid solution, which gradually absorbs hydrogen, converting to the Mg_2NiH_4 tetrahydride (a = 1.33 nm, b = 0.65 nm, c = 0.66 nm).

Our previous results on hydriding/nitriding of intermetallic compounds and alloys lead us to assume that the formation of Mg_2Ni-based hydride phases is accompanied by the incorporation of a certain amount of nitrogen into the metal matrix (we failed to find any experimental evidence for this assumption). In addition, it is well known that hydrogen exposure reduces the particle size of metallic systems. Therefore, given the above two circumstances, the formation of the magnesium hydride MgH_2 (a = 0.454 nm, c = 0.309 nm) and magnesium amide $Mg(NH_2)_2$ (a = 1.038 nm, c = 2.006 nm) at 150°C is attributable to the decomposition of the Mg_2NiH_4 tetrahydride, with the resultant magnesium metal entering into hydriding and amidation reactions. Note that all of the synthesized phases were stable under the experimental conditions of this study: according to X-ray diffraction data, all of the above compounds were among the reaction products after pressure release. The hydriding/nitriding process at 150°C further increases the specific surface area of the material (25.5 m^2/g). According to thermal analysis data, the decomposition temperatures of Mg_2NiH_4 and $Mg(NH_2)_2$ are 260 and 365°C, respectively, in agreement with earlier results [6, 12].

At a hydriding/nitriding temperature of 200°C, the reaction products did not contain the parent intermetallic compound, which was probably among the factors responsible for the drastic increase in the specific surface area of the material (to 113.3 m^2/g). Moreover, its diffraction pattern showed weak reflections characteristic of nickel nitride, Ni_3N.

As reported previously, massive nickel is nonreactive with ammonia, whereas fine-particle nickel reacts with it at 300–450°C to form Ni_3N. Therefore, the observed reflections from this nitride indicate that the decomposition of the Mg_2NiH_4 tetrahydride is accompanied by the formation of both magnesium and nickel, the latter entering into a nitriding reaction.

Note also that the decomposition of the Mg_2NiH_4 tetrahydride competes with disproportionation of this compound, as evidenced by the formation of another intermetallic compound, $MgNi_2$ (a = 0.482 nm, c = 1.597 nm), in the reaction at 200°C without NH_4Cl (sample 4). In addition, the reaction products contained metallic nickel (a = 0.353 nm) and the magnesium nitride Mg_3N_2 (a = 0.997 nm), which were the major products of the reaction between the intermetallic compound Mg_2Ni and ammonia at temperatures from 300 to 450°C (samples 6–10).

The presence of ammonium chloride in the reaction system leads to its reaction at relatively low temperatures (150–200°C) with the magnesium resulting from Mg_2NiH_4 decomposition and the formation of trace amounts of $MgCl_2$. After ammonia exposure of the parent intermetallic compound at 300°C and higher temperatures (samples 6–10), no magnesium chloride was detected among the reaction products.

Note that the hydriding/nitriding process yields magnesium amide even at 300°C (sample 7). At higher tem-

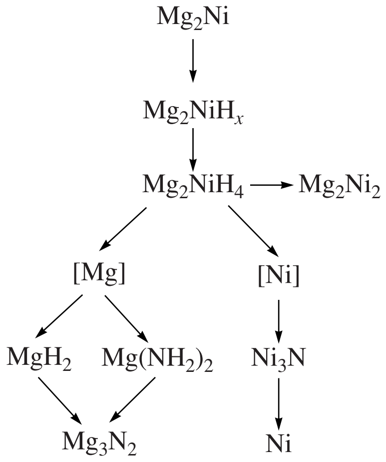
Conditions and products of the reaction between Mg_2Ni and ammonia

Sample no.	Synthesis conditions		Reaction products				
	t, °C	τ, h	phase composition	a, nm	b, nm	c, nm	S, m^2/g
1	100	32	Mg_2Ni	0.523	–	1.325	14.7
2	150	35	Mg_2Ni	0.519	–	1.449	25.5
			$Mg_2NiH_{0.3}$	0.525	–	1.349	
			Mg_2NiH_4	1.33	0.65	0.66	
			MgH_2	0.454	–	0.309	
			$Mg(NH_2)_2$	1.038	–	2.006	
3	200	26	$Mg(NH_2)_2$	1.037	–	2.019	113.3
			Mg_2NiH_4	1.33	0.65	0.66	
			Ni_3N (tr)				
4*	200	30	$Mg(NH_2)_2$	1.034	–	2.023	70.9
			Mg_3N_2	0.997	–	–	
			Ni	0.353	–	–	
			$MgNi_2$	0.482	–	1.597	
5	250	30	Ni	0.353	–	–	40.6
			amorphous phase				
6	300	28	Ni	0.353	–	–	20.0
			$Mg(NH_2)_2$	1.040	–	2.010	
7*	300	30	$Mg(NH_2)_2$	1.033	–	2.022	56.3
			Ni	0.353	–	–	
			Mg_3N_2	0.997	–	–	
8	350	28	Ni	0.353	–	–	5.0
			Mg_3N_2	0.997	–	–	
9	400	28	Ni	0.353	–	–	7.1
			Mg_3N_2	0.997	–	–	
10	450	30	Ni	0.353	–	–	1.8
			Mg_3N_2	0.997	–	–	
			Ni_3N (tr)				

* Exposure to ammonia without NH_4Cl.

peratures, this compound seems to decompose. It is reasonable to assume that the presence of $Mg(NH_2)_2$ among reaction products is responsible for the relatively large specific surface area of the material, 56.3 m^2/g at 300°C, which drops to 1.8 m^2/g as the process temperature is raised to 450°C.

It follows from the data in the table and from the scheme below that the parent intermetallic compound Mg_2Ni is hydrided by ammonia in the range 150–200°C with the formation of the Mg_2NiH_4 tetrahydride, which undergoes a number of chemical transformations at higher temperatures in ammonia atmosphere. The scheme illustrates the main chemical transformations of the parent intermetallic compound and indicates the reaction intermediates and final products.



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